

Structural and Electronic Characteristics of Thienyl(aryl)iodonium Triflates[†]

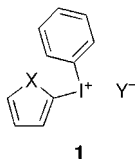
Darren Bykowski,[‡] Robert McDonald,[‡] Robert J. Hinkle,^{*,§} and Rik R. Tykwinski^{*,‡}

Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada, and Department of Chemistry, The College of William and Mary, P.O. Box 8795, Williamsburg, Virginia 23187-8795

Received July 10, 2001

A general strategy toward the synthesis of arylidonium triflate salts has been exploited to afford derivatives that incorporate thiophene and bithiophene components. Both mono- and bis(iodonium) salts have been realized, and a series of bithienyl(aryl)iodonium triflates with increasingly electron-withdrawing substituents on the aryl moiety have been synthesized. X-ray crystallographic analysis of four derivatives (**4a**, **4b**, **6b**, and **8c**) demonstrates that the solid-state organization of these salts incorporates extensive networks of secondary bonding interactions between the cationic idonium centers and the triflate counterions. UV–vis spectroscopic analysis shows that the electronic interactions between pendent aryl and heteroaryl groups across the idonium center can be dictated by substitution. Furthermore, the energy of the HOMO–LUMO gap decreases substantially in weakly or noncoordinating solvents.

Diaryl- and aryl(heteroaryl)iodonium salts are the most numerous and widely utilized class of iodine(III) compounds, due to their rich chemistry and practical applications.^{1–6} Heteroarylidonium derivatives **1**, de-



rived from furan, thiophene, selenophene, and pyrrole, have been reported, and a wide range of counterions (Y⁻) have also been incorporated.⁷ Although the chemistry and biochemistry of these compounds have been widely investigated, there are no reports of the electronic and structural characteristics for either the thienyl- or bithienylidonium salts.^{8–11}

Thiophene and oligothiophene compounds display unique electronic behavior and have substantial potential as organic materials for nonlinear optics, for electroluminescence, and as conducting polymers.¹² Whereas the thiophene scaffold has been incorporated into a variety of idonium salts (vide supra), the potential of these compounds as optical materials has, to the best of our knowledge, gone unnoticed. Several aspects of thienylidonium compounds intrigued us: (a) the ability of the idonium moiety to function as a π -electron acceptor, (b) the extent of π -electron communication (through I⁺) between the pendant aryl groups of the formally cross-conjugated idonium salt framework (Figure 1), and (c) the optical properties as a function of molecular structure. Reported herein are the syntheses of mono- and bis-[phenyl(iodonium)] triflate salts of thiophene and bithiophene and an evaluation of the physical and electronic characteristics of these molecules.

Results and Discussion

Thienyl(phenyl)iodonium salts **4a,b** were synthesized by the addition of idonium transfer reagent **3**¹³ to a CH₂Cl₂ solution of the respective heteroarylstannane

* To whom correspondence should be addressed. Email: rik.tykwinski@ualberta.ca.

[†] Dedicated to Professor Peter J. Stang on the occasion of his 60th birthday.

[‡] University of Alberta.

[§] The College of William and Mary.

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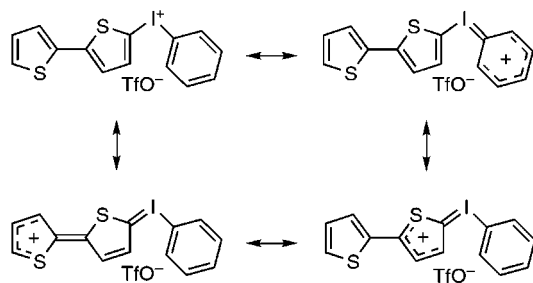
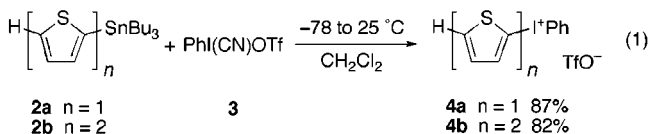
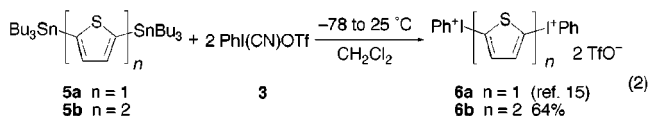


Figure 1. Cross-conjugated interactions for a bithienyl(aryl)iodonium salt.

2a,b at $-78\text{ }^{\circ}\text{C}$ (eq 1).¹⁴ The reaction mixture was warmed to room temperature, and hexanes were added



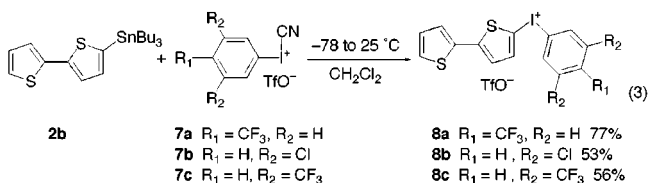
to crystallize the iodonium salts from solution. In a similar manner, heteroaryl(distannanes) **5a,b** were reacted with 2 equiv of reagent **3** in CH_2Cl_2 at $-78\text{ }^{\circ}\text{C}$ (eq 2). Upon warming, the less soluble bis(iodonium) salts



6a,b began to precipitate from solution. After the suspension had been warmed to room temperature, the addition of hexanes and ether completed precipitation of **6a,b**.¹⁵

The iodonium salts **4a,b** and **6a,b** were filtered, washed with hexanes, and dried under vacuum. If necessary, removal of any remaining stannane impurities was accomplished by recrystallization of the iodonium salt from a concentrated CH_3CN solution by the addition of Et_2O and hexanes.

The third series of thienyliodonium salts was derived from the reaction of bithienylstannane **2b** with functionalized iodonium transfer reagents **7a–c** (eq 3).^{13,14} These reactions proceeded in a manner analogous to the formation of **4b**, affording dithienyl salts **8a–c** in 53–77% yields as yellow solids.



Iodonium salts **4a,b**, **6a,b**, and **8a–c** are stable solids that can be stored for months under ambient conditions if kept from light. As solids or in solution, however, the iodonium salts slowly decompose in the presence of light. Thermally, the salts show reasonable stability and decomposition points rather than melting points. For

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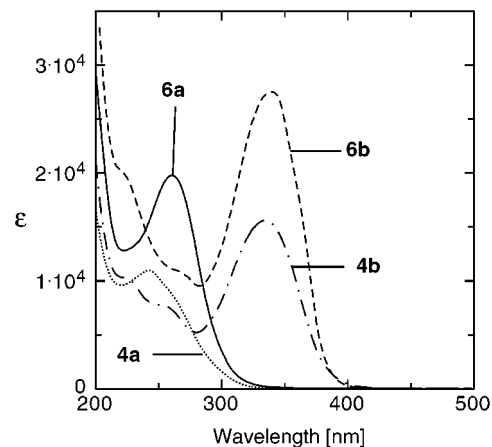


Figure 2. Electronic absorption spectra (ϵ [$\text{L M}^{-1} \text{cm}^{-1}$]) in CH_3CN comparing heteroaryl(aryl)iodonium salts **4a,b** and **6a,b**.

example, bis(iodonium) salts **6a**¹⁵ and **6b** decompose at 137–138 and 193–194 $^{\circ}\text{C}$, respectively, whereas dithienyliodoniums **4b** and **8a–c** all decompose between 81 and 92 $^{\circ}\text{C}$.

All heteroaryl(iodonium) triflates were fully characterized by multinuclear NMR and IR spectroscopies, mass spectrometry, and, in several cases (vide infra), X-ray crystallographic analysis of single crystals. In the electrospray mass spectrum (positive mode, 3:1 $\text{MeOH}/\text{toluene}$) for each salt, the molecular peak of the monocationic portion of the salt $[\text{M} - \text{TfO}^-]^+$ is clearly observed. The IR spectra show the C–H stretching absorptions of the respective heterocyclic moieties between 3070 and 3095 cm^{-1} and of the triflate anion at ca. 1240, 1160, and 1025 cm^{-1} . The ^1H NMR spectra display characteristic heteroaromatic resonances between 8.1 and 7 ppm, as well as a pseudo-first-order doublet–triplet–triplet resonance pattern typical of an iodonium phenyl group for **4a,b** and **6a,b**. The ^{13}C NMR spectra are consistent with the proposed structures, including the resonances of triflate moieties as quartets ($^1J_{\text{CF}} = 320$ Hz), centered at ca. 120 ppm. Particularly conspicuous in the ^{13}C NMR spectra are the shielded *ipso*-carbons ($\text{I}^+ - \text{C}$) of the phenyl and heteroaryl moieties, resonating near δ 117 and 93, respectively.¹⁶ The triflate anion of each product was also confirmed by a singlet at ca. -78 ppm in the ^{19}F NMR spectrum.

Electronic Characteristics. A comparison of the linear electronic absorption behavior of **4a,b** and **6a,b** in CH_3CN is shown in Figure 2. The most obvious feature is the greater molar absorptivity for bis(iodonium) salts **6a** and **6b** vs mono(iodonium) salts **4a** and **4b**. In addition, λ_{max} values for the bis(iodonium) salts (**6a**, 260 nm; **6b**, 343 nm) are red-shifted compared to those for the mono(iodonium) salts (**4a**, 242 nm; **4b**, 334 nm).

An empirical measure of iodonium cross conjugation can be approximated by comparing the electronic spectrum of the salt, e.g., **4b**, to that of its constituent parts (Figure 3). In comparison to that for bithiophene ($\lambda_{\text{max}} = 303$ nm), λ_{max} for 5-iodobithiophene is red-shifted 12 nm to 315 nm ($\epsilon = 14900$), as one would expect from the addition of the polarizable heteroatom to the conjugated bithienyl framework. The absorption spectrum for iodo-

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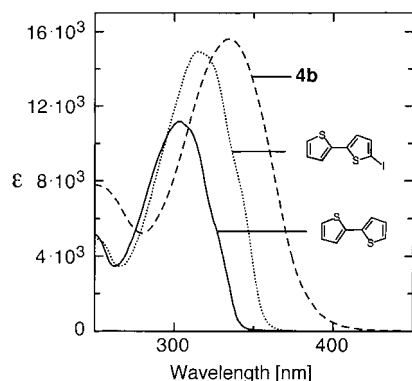


Figure 3. Electronic absorption spectra (ϵ [$\text{L M}^{-1} \text{cm}^{-1}$]) in CH_3CN comparing 2,2'-bithiophene, 5-iodo-2,2'-bithiophene, and **4b**.

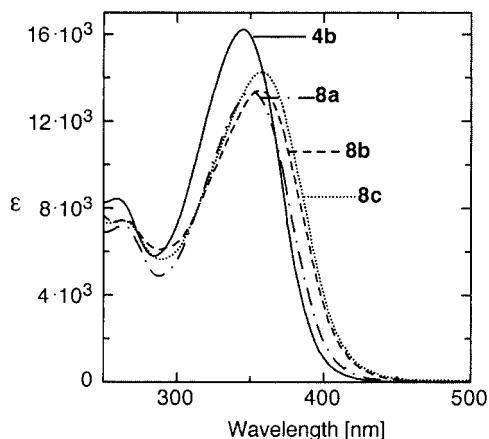


Figure 4. Electronic absorption spectra (ϵ [$\text{L M}^{-1} \text{cm}^{-1}$]) in CH_2Cl_2 comparing bithienyl(aryl)iodonium salts **4b** and **8a–c**.

nium salt **4b** shows λ_{max} at 334 nm (15600), 19 nm lower in energy than λ_{max} for 2-iodobithiophene. When measured in CH_2Cl_2 , the difference is even greater: λ_{max} for **4b** (345 nm) is red-shifted by 28 nm vs that for 5-iodobithiophene (317 nm). The disparity in λ_{max} values between an iodonium salt and its components is more substantial for the mono(iodonium) salts **4a** and **4b** than for bis(iodonium) derivatives **6a** and **6b** (not shown), and may indicate a saturation of the donating ability of the (bi)thienyl group in the presence of two electron-withdrawing I^+ groups in **6a,b**.¹⁷ For example, λ_{max} of bis(iodonium) **6b** (340 nm) is shifted by only 8 nm vs that of 5,5'-diiodo-2,2'-bithiophene (332 nm). It is clear, however, that electronic communication via the d-orbitals of the cationic I(III) linker(s) is occurring for thienyliodonium salts. Beringer has reported a similar trend for diaryliodonium salts with electron-releasing functionality attached to aryl groups (i.e., OH, OR, NH_2).¹⁰ Thus, in the present case, the data suggest that as one progresses from the thienyl to the bithienyl group, there is an increased role of the heteroaromatic substituent as an electronic donor moiety to the electron-deficient I^+ center.

Figure 4 demonstrates the influence of the pendant aryl groups on the cross-conjugated donor–acceptor relationship for bithienyl salts **4b** and **8a–c**. In the presence of the electron-rich bithienyl moiety, the mag-

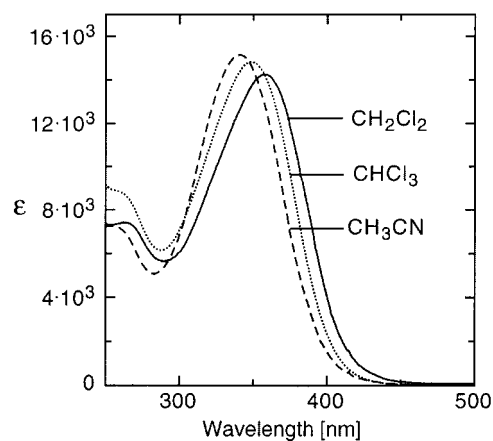


Figure 5. Electronic absorption spectra (ϵ [$\text{L M}^{-1} \text{cm}^{-1}$]) of **8c** in CH_2Cl_2 , CHCl_3 , and CH_3CN .

nitude of the interaction at or across the iodonium bridge is augmented as the electron-deficient character of the aryl group is increased. As measured in CH_2Cl_2 , the value of λ_{max} is consistently red-shifted from 345 nm for **4b** to 351 nm for **8a** to nearly equal values of 357 and 358 nm, respectively, for **8b** and **8c**.

The solvatochromism of bithienyliodonium salts **4b** and **8a–c** was measured in a range of solvents of varied polarity.¹⁷ For iodonium salt **4b**, for example, λ_{max} values remain approximately constant at ca. 334 nm in solvents with the ability to coordinate and solvate the positively charged I(III) group (Et_2O , THF, and CH_3CN); the λ_{max} energy is red-shifted by ca. 10 nm to 345 nm when measured in noncoordinating solvents such as CH_2Cl_2 and CHCl_3 . This effect is even more dramatic for **8a–c**, as the donor–acceptor interactions are enhanced by the presence of the increasingly electron-poor aryl substituents. Iodonium salt **8c** shows the most dramatic solvatochromic shift, with λ_{max} changing from 341 nm in CH_3CN to 358 nm in CH_2Cl_2 (Figure 5). Thus, the HOMO–LUMO gap of the bithienyliodonium salts is clearly solvent dependent, but it appears that the extent of this effect is primarily a function of the solvating ability of the solvent, as opposed to polarity.⁹

An alternative interpretation of the above results could include solution-state aggregation of the iodonium triflate salts, similar to that observed for these compounds in the solid state (vide infra). A number of observations would argue against this possibility. The electronic absorption spectra of representative iodonium salts (**4a**, **6b**, and **8a**) were measured over concentrations accessible by the detection range of our spectrophotometer (10^{-4} to 10^{-5} M) and in CH_3CN and CH_2Cl_2 .¹⁷ All measurements were found to obey Beer's law. Furthermore, the addition of Bu_4NOTf (1–100 equiv) to solutions of mono- or bis(iodonium) salts produced no change in the λ_{max} values, irrespective of the solvent employed. Thus, it seems unlikely that aggregation or ion pairing plays a major role in altering the absorption energies. Rather, the observed absorption characteristics are consistent with changes to the HOMO–LUMO energies derived from alterations in the electronic structure of the cationic portion, achieved via tuning of the molecular structure.

Solid-State Characteristics. Recent reports have suggested a significant role of secondary bonding interactions for the two- and three-dimensional organization of

(17) These UV–vis spectra are supplied as Supporting Information.

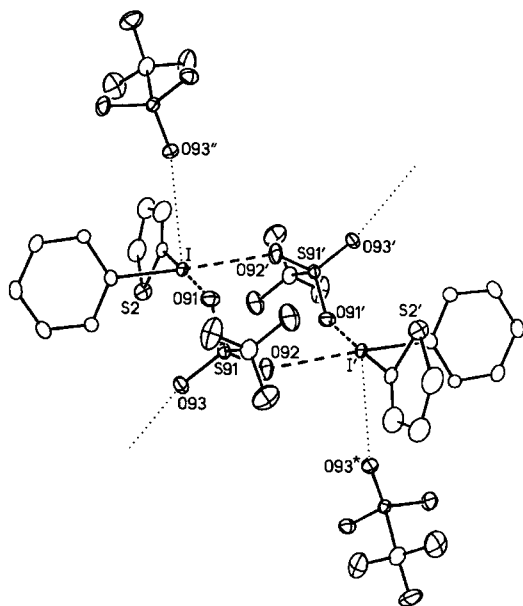


Figure 6. X-ray crystal structure of **4a** illustrating the extended linkages between iodonium cations through the triflate anions (20% probability level).

iodonium salts.^{18,19} As solid-state orientation influences most optical materials applications, the structural characteristics of **4a**, **b**, **6b**, and **8c** were investigated by X-ray crystallography. The ionic nature of the iodonium salts predisposes them toward crystallinity, and large single crystals (millimeters to a side) were easily obtained under ambient conditions, in the dark, by the slow diffusion of hexanes into CH₃CN/Et₂O solutions.

The ORTEP diagram in Figure 6 for **4a** shows the weak, nonbonded interactions between each positively charged iodine and the oxygens of three nearby triflates. The interactions of I with O(91) and O(92') (shown with dashed lines) at 2.822(3) and 2.873(3) Å are similar in length, giving an approximately square planar coordination geometry, as has been observed for other iodonium salts.² The third I⋯O interaction, with O(93'') (dotted line), is significantly weaker at 3.342(3) Å, defining an overall square pyramidal geometry about iodine. The strongest associations are therefore formed among dimeric pairs of iodonium and triflate ions located near a crystallographic inversion center such that the atoms I, O(91), S(91), and O(92) and their inversion-generated counterparts I', O(91'), S(91'), and O(92') form an eight-membered ring centered about the crystallographic origin and inversion center (0, 0, 0).²⁰ Weaker interactions between O(93) (and its symmetry-generated counterpart O(93')) as well as O(93'') and O(93'') and nearby iodine atoms (dotted lines) link adjacent dimeric units into an extended lattice.

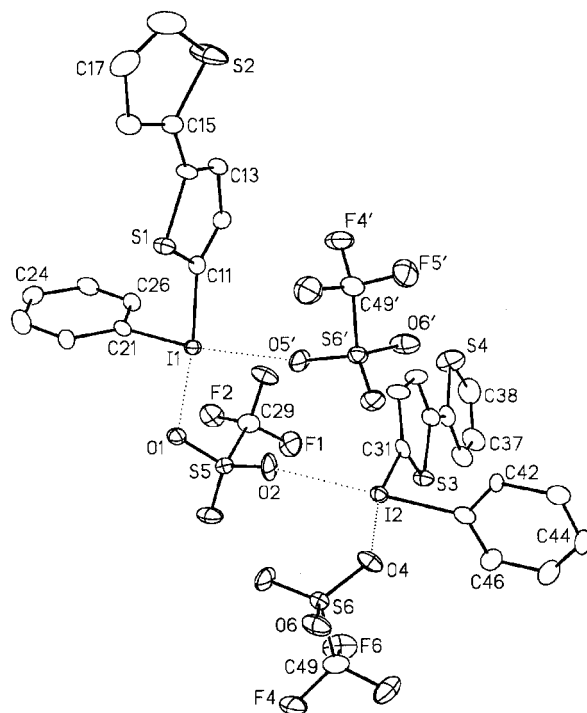


Figure 7. X-ray crystal structure of **4b** illustrating nonbonded interactions (20% probability level).

In addition to two crystallographically independent cationic iodonium moieties, the crystal lattice of **4b** incorporates half of a hexane molecule per asymmetric unit. An ORTEP diagram of **4b** is shown in Figure 7 and illustrates the relative orientation of the two cations, as well as nonbonded interactions with the triflate ions; the hexane solvent molecule has been omitted for clarity. Each positively charged iodine shows weak nonbonded interactions with an oxygen of two nearby triflates. The interactions of I(1) with O(1) and O(5') (shown as dotted lines) at 2.779(6) and 2.869(8) Å and of I(2) with O(2) and O(4) at 2.843(8) and 2.743(7) Å are similar in length, giving the approximately square planar coordination geometry about each I(III) center as observed for **4a**. Unlike structure **4a**, however, a third nonbonded interaction between I⁺ and a triflate oxygen is absent. The crystallographically independent bithiophenes also show different relative geometries. Whereas the two individual thienyl moieties of the bithiophene bonded to I(2) are essentially coplanar, in the other molecule the thiophenes are rotated approximately 15° from coplanarity.

Bis(iodonium) salt **6b** crystallizes in the tetragonal crystal system with two crystallographically independent molecules in the unit cell (Figure 8). For each of the two unique molecules in the solid state, secondary interactions are clearly evident between iodine and the triflate oxygens with distances of I(1)⋯O(31) and I(1)⋯O(32'') at 2.766(4) and 2.801(4) Å, respectively, in molecule 1 and I(2)⋯O(41) and I(1)⋯O(42*) at 2.752(4) and 2.859(3) Å, respectively, in molecule 2. The apical I⋯O interaction observed in **4a** is again absent in **6b**.

Interestingly, the overall solid-state structure of **6b** is composed of two independent and interpenetrating iodonium networks, each constructed from one set of the crystallographically unique molecules shown in Figure 8. There are no secondary interactions (other than van der Waals forces) between the two networks, e.g., no coordination of I(1) to O(41)/O(42)/O(43). A dissection of

(18) Zhdankin, V. V.; Kopusov, A. E.; Smart, J. T.; Tykwinski, R. R.; McDonald, R.; Morales-Izquierdo, A. *J. Am. Chem. Soc.* **2001**, *123*, 4095–4096.

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(20) For a similar dimeric example see: Maas, G.; Regitz, M.; Moll, U.; Rahm, R.; Krebs, F.; Hector, R.; Stang, P. J.; Crittall, C. M.; Williamson, B. L. *Tetrahedron* **1992**, *48*, 3527–3540.

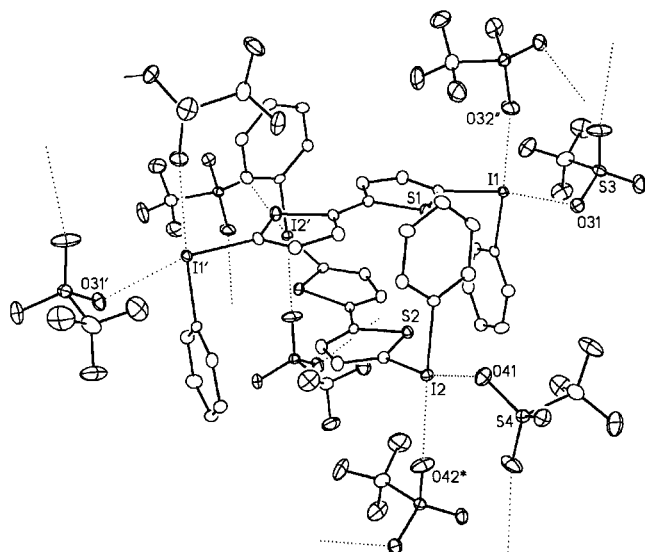


Figure 8. X-ray crystal structure of **6b** showing both of the crystallographically independent molecules and nonbonded interactions that define two interpenetrating networks, as described in the text (20% probability level).

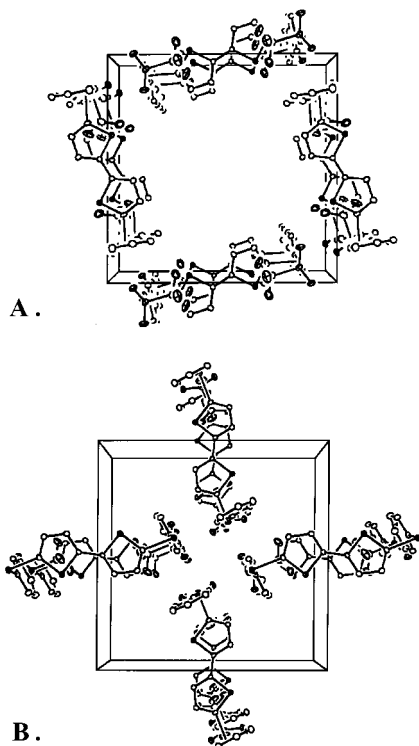


Figure 9. Crystal packing diagrams for **6b** as viewed down the *c* axis showing the individual networks: (A) only the iodonium salts composed of I(1); (B) only the iodonium salts composed of I(2) (as well as the associated phenyl and bithienyl groups in each case).

these two networks, i.e., a crystal packing diagram of each crystallographically independent molecule, is displayed in Figure 9. Each is viewed along the crystal *c* axis.²¹

Bis(iodonium) salt **8c** crystallizes in the triclinic crystal system with two crystallographically independent mol-

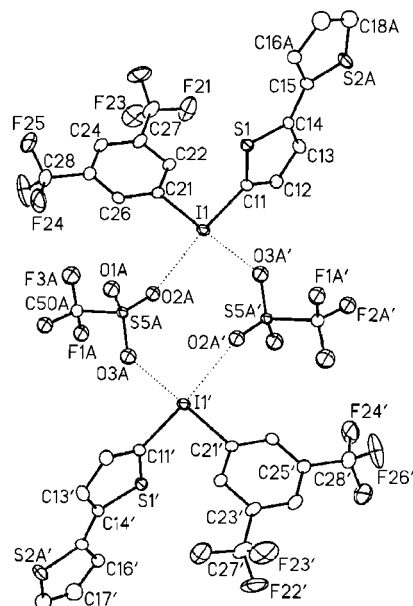


Figure 10. Perspective view of one of the crystallographically independent molecules of **8c** (and its symmetry-related neighbor) and secondary bonding to nearest-neighbor triflate ions (20% probability level).

ecules in the unit cell, one of which is shown in Figure 10. The secondary interactions of I(1) with O(2A) and O(3A) (shown with dotted lines) at 2.770(8) and 2.788(8) Å (2.863(4) and 2.872(4) Å for the other independent molecule, not shown) are nearly identical in length, again giving an approximately square planar coordination geometry. Unlike the related bithienyliodonium salt **4b**, secondary bonding interactions between two symmetry-related molecules of **8c** afford a dimer in the solid state. Interestingly, the structure of **8c** shows both a cisoid (not shown; see the Supporting Information) and a transoid (as shown in Figure 10) orientation of the two thiophene subunits of the bithienyl moiety, in a 25%:75% ratio, respectively. The structure of **4b**, on the other hand, is exclusively transoid.

Summary and Conclusions

Mono- and bis(aryl)heteroaryliodonium triflate salts can be conveniently prepared in good yields via the reaction of heteroarylstannanes and the appropriate iodonium transfer reagent. These stable, crystalline iodonium salts show highly organized two- and three-dimensional structure in the solid state that is directed by secondary bonding interactions. The hypervalent iodine moiety in thienyl- and bithienyliodonium salts can function as a conduit for electronic communication between pendant aryl and heteroaryl groups as demonstrated by UV-vis spectroscopy. These cross-conjugated, donor-acceptor interactions across the positively charged iodonium center are influenced by substitution as demonstrated by UV-vis spectroscopic analysis as a function of increased electron-withdrawing ability of pendant aryl groups in the presence of the electron-rich bithiophene moiety.

Experimental Section

Unless otherwise noted, reagents and solvents were used as received from commercial suppliers and reactions were

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performed under a N₂ atmosphere. CH₂Cl₂ and CH₃CN were distilled from CaH₂ prior to use. Compounds **2a**,²² **3**,¹³ **5a**,²³ **6a**,¹⁵ and **7a–c**¹⁴ were prepared as reported.

X-ray crystal data for **4a** (C₁₁H₈F₃IO₃S₂): monoclinic, space group *P*2₁/*c* (no. 14), *D*_c = 1.980 g cm⁻³, *Z* = 4, *a* = 12.3781(5) Å, *b* = 10.3986(4) Å, *c* = 12.4170(5) Å, β = 113.695(3)°, *V* = 1463.52(10) Å³. Final *R*(*F*) = 0.026; *wR*₂(*F*²) = 0.061 for 199 variables and 1984 data with *F*_o² ≥ -3σ(*F*_o²) (1805 observations [*F*_o² ≥ 2σ(*F*_o²)]).

X-ray crystal data for **4b**·(1/2)*n*-C₆H₁₄ (C_{16.5}H_{13.5}F₃IO₃S₃): monoclinic, space group *C*2/*c* (no. 15), *D*_c = 1.788 g cm⁻³, *Z* = 16, *a* = 20.4976(14) Å, *b* = 12.9866(14) Å, *c* = 31.366(2) Å, β = 106.091(5)°, *V* = 8022.3(12) Å³. Final *R*(*F*) = 0.0577; *wR*₂(*F*²) = 0.211 for 487 variables and 5132 data with *F*_o² ≥ -3σ(*F*_o²) (4448 observations [*F*_o² ≥ 2σ(*F*_o²)]).

X-ray crystal data for **6b** (C₂₂H₁₄F₆I₂O₆S₄): tetragonal, space group *P*4̄ (no. 81), *D*_c = 2.020 g cm⁻³, *Z* = 4, *a* = 14.8510(5) Å, *c* = 12.9769(6) Å, *V* = 2862.08(19) Å³. Final *R*(*F*) = 0.0297; *wR*₂(*F*²) = 0.0612 for 361 variables and 5442 data with *F*_o² ≥ -3σ(*F*_o²) (4941 observations [*F*_o² ≥ 2σ(*F*_o²)]).

X-ray crystal data for **8c** (C₁₇H₈F₉IO₃S₃): triclinic, space group *P*1̄ (no. 2), *D*_c = 1.957 g cm⁻³, *Z* = 4, *a* = 13.0926(8) Å, *b* = 13.9652(8) Å, *c* = 14.2829(8) Å, α = 115.9518(11)°, β = 105.9978(12)°, γ = 91.9782(13)°, *V* = 2220.6(2) Å³. Final *R*(*F*) = 0.0462; *wR*₂(*F*²) = 0.1304 for 595 variables and 8917 data with *F*_o² ≥ -3σ(*F*_o²) (6914 observations [*F*_o² ≥ 2σ(*F*_o²)]).

(2-Thienyl)iodonium Triflate (4a). To a stirred solution of tributylthienylstannane **2a**²² (1.71 g, 4.58 mmol) in CH₂Cl₂ (5 mL) at -78 °C under nitrogen was added reagent **3** (1.74 g, 4.59 mmol). The mixture was warmed to rt and stirred for 1 h. A small amount of residual white solid was removed by filtration through a plug of glass wool. The product was then precipitated from solution by the addition of ether and hexanes, filtered, and washed with ether to give **4a** (1.75 g, 87% yield) as a colorless microcrystalline solid. Mp: 137–139 °C dec. UV-vis: λ_{max} (ε) (CH₂Cl₂) 245 (9350), (CHCl₃) 242 (10000), (CH₃CN) 242 (11000) nm. IR (CH₂Cl₂ cast): 3091, 1244, 1162, 1024 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.87 (dd, *J* = 4.0, 1.3 Hz, 1H), 7.72 (dd, *J* = 5.6, 1.3 Hz, 1H), 7.61 (t, *J* = 8.5 Hz, 1H), 7.47 (t, *J* = 8.5 Hz, 2H), 7.14 (dd, *J* = 5.6, 4.0 Hz, 1H). ¹³C NMR (125.7 MHz, CDCl₃): δ 141.6, 137.7, 133.9, 132.6, 132.4, 130.3, 120.2 (q, *J* = 320 Hz, CF₃SO₃⁻), 117.7, 95.1. ESI HRMS (3:1 CH₃OH/toluene): calcd for C₁₀H₈IS 286.9391, found 286.9393 ([M - TfO]⁺).

Phenyl[5-(2,2'-bithienyl)]iodonium Triflate (4b). To a stirred CH₂Cl₂ (15 mL) solution of tributylthienylstannane²³ **2b** (0.10 g, 0.22 mmol) at -78 °C under nitrogen was added reagent **3** (0.080 g, 0.21 mmol). The mixture was warmed to rt and stirred for 30 min. The now green solution was cooled to -78 °C, and ether and hexanes were added to produce a green slurry which was stirred at -78 °C for 30 min. The light green solid was filtered on a fritted funnel and washed with cold (-78 °C) hexanes and ether. Recrystallization from a minimal amount of CH₂Cl₂ by the addition of ether and hexanes gave **4b** (0.090 g, 82% yield) as a light yellow solid. Mp: 81–82 °C dec. UV-vis λ_{max} (ε): (Et₂O) 333 (14500), (THF) 332 (16600), (CH₂Cl₂) 345 (16200), (CHCl₃) 344 (16300), (CH₃CN) 334 (15600) nm. IR (CH₂Cl₂ cast): 3091, 1242, 1167, 1063 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 3.9, 1H), 7.57 (t, *J* = 8.5 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.32 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.21 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.09 (d, *J* = 3.9 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.9 Hz, 1H). ¹³C NMR (75.5 MHz, CDCl₃): δ 149.6, 142.6, 134.2, 132.4, 132.2, 128.4, 127.3, 126.4, 125.6, 120.2 (q, *J* = 320 Hz, CF₃SO₃⁻), 117.7, 92.4 (one degenerate signal). ESI MS (3:1 CH₃OH/toluene): *m/z* 368.9 ([M - TfO]⁺, 100).

Bis(iodonium) Ditriflate 6a. The spectral data are consistent with those reported.¹⁵ UV-vis λ_{max} (ε): (CH₃CN) 260 (19000) nm.

Bis(iodonium) Ditriflate 6b. To a stirred CH₂Cl₂ (15 mL) solution of **5b** (0.600 g, 0.805 mmol)²³ under nitrogen at -78 °C was added reagent **3** (0.610 g, 1.61 mmol). The mixture was warmed to rt and stirred for 1 h, resulting in a tan-colored suspension. Ether and hexanes were added to complete precipitation, and the solid was filtered and washed with ether. Recrystallization from a minimal amount of CH₃CN by the addition of ether and hexanes gave **6b** (0.448 g, 64% yield) as a tan solid. Mp: 132–133 °C dec. UV-vis λ_{max} (ε): (CH₃CN) 340 (27300) nm. IR (CH₂Cl₂ cast): 3090, 1239, 1170, 1027 cm⁻¹. ¹H NMR (300 MHz, CD₃CN): δ 8.09 (d, *J* = 8.5 Hz, 4H), 7.92 (d, *J* = 4.2 Hz, 2H), 7.71 (t, *J* = 8.5 Hz, 2H), 7.54 (t, *J* = 8.5 Hz, 4H), 7.36 (d, *J* = 4.2 Hz, 2H). ¹³C NMR (75.5 MHz, CD₃CN): δ 143.9, 135.8, 134.3, 133.6, 129.6, 96.4 (three peaks not observed). ESI MS (3:1 CH₃OH/toluene): *m/z* 892.8 ([M + Na]⁺, 7), 720.9 ([M - TfO]⁺, 54).

General Procedure for 8a–c. To a stirred solution of **2b** (1.2–1.5 equiv) in CH₂Cl₂ (5–10 mL) under nitrogen at -78 °C was added the appropriate transfer reagent **7a–c** (0.100 g). The solution was stirred for 10 min, briefly warmed to rt, and cooled to -78 °C, and hexanes were added to precipitate out a light yellow slurry. The mixture was kept at -78 °C and stirred for 40 min. The impure solid was filtered off, dissolved in a minimal amount of CH₂Cl₂, and recrystallized by the addition of hexanes to afford the respective iodonium salt **8a–c**.

4-(Trifluoromethyl)phenyl[5-(2,2'-bithienyl)]iodonium Triflate (8a). Tributylstannane **2b** (0.150 g, 0.329 mmol) was reacted with **7a** (0.100 g, 0.224 mmol) as per the general procedure to give **8a** (0.101 g, 77%) as a yellow solid. Mp: 82–83 °C dec. UV-vis λ_{max} (ε): (CH₂Cl₂) 351 (13400), (CHCl₃) 348 (13500), (CH₃CN) 337 (14000) nm. IR (CH₂Cl₂ cast): 3093, 1324, 1243, 1048 cm⁻¹. ¹H NMR (300 MHz, CD₃CN): δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 4.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.50 (dd, *J* = 1.0, 5.1 Hz, 1H), 7.37 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.28 (d, *J* = 4.0 Hz, 1H), 7.10 (dd, *J* = 5.1, 3.7 Hz, 1H). ¹³C NMR (75.5 MHz, CD₃CN): δ 151.0, 144.8, 136.1, 134.7, 134.7 (q, *J* = 33.3 Hz), 129.9 (q, *J* = 3.7 Hz), 129.7, 129.1, 127.9, 126.9, 124.3 (q, *J* = 272 Hz, CF₃), 121.9 (q, *J* = 320 Hz, CF₃SO₃⁻), 121.7, 92.9. ¹⁹F NMR (376.5 MHz, CD₃CN): δ -63.4 (CF₃), -78.4 (CF₃SO₃⁻). ESI HRMS: calcd for C₁₅H₉F₃S₂I 436.9143, found 436.9144 ([M - TfO]⁺).

3,5-Dichlorophenyl[5-(2,2'-bithienyl)]iodonium triflate (8b). Tributylstannane **2b** (0.150 g, 0.329 mmol) was reacted with **7b** (0.100 g, 0.223 mmol) as per the general procedure to give **8b** (0.070 g, 53%) as a yellow solid. Mp: 91–92 °C dec. UV-vis λ_{max} (ε): (CH₂Cl₂) 357 (13400), (CHCl₃) 351 (13500), (CH₃CN) 342 (13800) nm. IR (CH₂Cl₂ cast): 3072, 1408, 1239, 1167, 1025 cm⁻¹. ¹H NMR (300 MHz, CD₃CN): δ 8.09 (d, *J* = 1.9 Hz, 2H), 7.93 (d, *J* = 4.2 Hz, 1H), 7.73 (t, *J* = 1.9 Hz, 1H), 7.49 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.37 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.27 (d, *J* = 4.2 Hz, 1H), 7.10 (dd, *J* = 5.1, 3.6 Hz, 1H). ¹³C NMR (75.5 MHz, CD₃CN): δ 151.3, 145.1, 137.9, 134.7, 134.3, 133.6, 129.7, 129.2, 128.0, 127.0, 122.2 (q, *J* = 320 Hz, CF₃SO₃⁻), 117.1, 92.9. ¹⁹F NMR (376.5 MHz, CD₃CN): δ -78.4. ESI HR-MS: calcd for C₁₄H₈Cl₂ISO₂ 436.8491, found 436.8488 ([M - TfO]⁺).

3,5-Bis(trifluoromethyl)phenyl[5-(2,2'-bithienyl)]iodonium Triflate (8c). Tributylstannane **2b** (0.120 g, 0.264 mmol) was reacted with **7c** (0.100 g, 0.194 mmol) as per the general procedure to give **8c** (71 mg, 56%) as a yellow solid. Mp: 86–87 °C dec. UV-vis λ_{max} (ε): (CH₂Cl₂) 358 (14200), (CHCl₃) 348 (14800), (CH₃CN) 341 (15200) nm. IR (CH₂Cl₂ cast): 3074, 1343, 1278, 1027 cm⁻¹. ¹H NMR (300 MHz, CD₃CN): δ 8.68 (br s, 2H), 8.30 (br s, 1H), 7.99 (d, *J* = 4.1 Hz, 1H), 7.51 (br d, *J* = 5.1 Hz, 1H), 7.39 (d, *J* = 3.8 Hz, 1H), 7.29 (d, *J* = 4.1 Hz, 1H), 7.11 (dd, *J* = 5.1, 3.8 Hz, 1H). ¹³C NMR (75.5 MHz, CD₃CN): δ 151.4, 145.3, 136.4 (q, *J* = 3.5 Hz), 134.7 (q, *J* = 34.7 Hz), 134.7, 129.7, 129.2, 128.1 (sept, *J* = 3.6 Hz), 128.1, 126.9, 123.1 (q, *J* = 273.1 Hz, CF₃), 121.8 (q, *J* = 320.4 Hz, CF₃SO₃⁻), 117.8, 92.9. ¹⁹F NMR (376.5 MHz, CD₃CN): δ

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−63.2 (CF_3), −78.8 (CF_3SO_3^-). ESI HR-MS: calcd for $\text{C}_{16}\text{H}_8\text{F}_6\text{IS}_2$ 504.9018, found 504.9021 ($[\text{M} - \text{TfO}^-]^+$).

Acknowledgment. This work was supported by the University of Alberta, ASRA, the National Sciences and Engineering Research Council of Canada, the Research Corp. (Grant CC4659 to R.J.H.), and the National

Science Foundation (CAREER, Grant CHE-9983863 to R.J.H.).

Supporting Information Available: General experimental details, X-ray crystallographic details for compounds **4a**, **4b**, **6b**, and **8c**, and numerous electronic absorption spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO015910T